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Katsuya ITO, et al.

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TRANSLATOR'S DECLARATION

Honorable Commissioner for Patents

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Sir:

I, Ritsuko Arimura, declare:

That I am well acquainted with both the Japanese and English languages;

That the attached document represents a true English translation of Japanese Patent Application No. 2003-295636 filed on August 19, 2003; and

That I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 14th day of November, 2007.


Ritsuko Arimura

(Translation)

J A P A N P A T E N T O F F I C E

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Applicant(s)	: Toyo Boseki Kabushiki Kaisha

Commissioner, Japan Patent Office

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【List of the Annexed Documents】
 【Document】 Claims One copy
 【Document】 Specification One copy
 【Document】 Abstract One copy
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【Document】 Claims

【Claim 1】

A polyester film comprising a substrate film having an initial elastic modulus in at least one direction of 2.5 - 10
5 GPa, an impact strength of 40 - 10000 J/mm and a thermal shrinkage in at least one direction at 150°C of -0.5% to 6%, and an easily adhesive coating layer on at least one surface of the substrate film, which shows a haze of 0.001% to 7%.

【Claim 2】

10 The polyester film of claim 1, wherein the thermal shrinkage in the longitudinal direction and the transverse direction of the substrate film at 150°C is each 0% to 4%.

【Claim 3】

The polyester film of claim 1 or 2, wherein the substrate
15 film is made of a polyester resin composition comprising 10 - 90 wt% of polyethylene terephthalate resin (A), and 90 - 10 wt% of a polybutylene terephthalate resin and/or polytrimethylene terephthalate resin (B).

【Claim 4】

20 The polyester film of claim 1, 2 or 3, wherein the substrate film has a reduced viscosity of not less than 0.80.

【Claim 5】

The polyester film of claim 1, 2, 3 or 4, wherein the easily
25 adhesive coating layer is composed of a coating solution comprising at least binder (C) and hardener (D).

【Claim 6】

The polyester film of claim 1, 2, 3, 4 or 5, which is obtained
30 by applying a coating solution for forming the aforementioned easily adhesive coating layer, and then subjecting the resulting film to at least uniaxial orientation.

【Claim 7】

The polyester film of claim 1, 2, 3, 4, 5 or 6, which is used
as a packaging material.

【Document】 Specification

【Title of the Invention】 Polyester Film

【Technical Field】

【0001】

5 The present invention relates to a polyester film with stable impact resistance, pinhole resistance and gas barrier property in boil treatment, which is suitable for food packaging and mold processing.

【Background Art】

10 【0002】

 Polyester films represented by polyethylene terephthalate resin have been extensively applied to various uses in view of the mechanical property, heat resistance and the like. However, they are not suitable for some uses because
15 of the inferiority in flexibility and molding processibility. On the other hand, since polyamide films represented by 6-nylon are superior in flexibility, pinhole resistance and gas barrier property, they are applied to many uses such as food packaging materials and the like. However, due to poor dimensional
20 stability against moisture absorption, they cannot be easily applied to boiling and retort food uses and industrial uses.

【0003】

 Therefore, polyester films having flexibility, which is one of the features of polyamide, have been considered. Most
25 of them acquire flexibility based on the use of a polyester copolymer in a part or the entirety of the substrate resin. However, since they show degraded mechanical strength and elastic modulus, problems may occur during post-processing such as printing and the like.

30 【0004】

 In view of the above, a flexible film made from crystalline polyester has been studied and, for example, films comprising polyethylene terephthalate resin and polybutylene terephthalate resin are known (Patent References 1, 2, 3).

【0005】

However, since these films are free of an easily adhesive coating layer, problems occur in that easily adhesive property of ink becomes degraded, stability of gas barrier property becomes defective after boiling treatment and the like, since a vapor-deposited layer formed of metal or inorganic oxide shows poor adhesion and so forth. In addition, problems of whitening and the like occur unless conditions for forming an easily adhesive coating layer are optimized.

10 【Patent reference 1】 JP-A-2002-037993

 【Patent reference 2】 JP-A-2002-179892

 【Patent reference 3】 JP-A-2002-321277

 【Disclosure of the Invention】

 【Problems to be Solved by the Invention】

15 【0006】

 The present invention has been made in view of the problems of the above-mentioned conventional films, and provides a polyester film superior in mechanical strength, heat resistance, chemical resistance, insulation property and thermal dimensional stability, and suitable for application to fields associated with boiling or retort treatment, which require tenacity, pinhole resistance, bending resistance, bag breakage resistance on dropping, impact resistance and the like, fields requiring thermoforming or vacuum forming, and various uses such as packaging bags for water-containing food, pharmaceutical products and the like.

 【Means of Solving the Problems】

 【0007】

 To achieve the above-mentioned object, the polyester film of the present invention has a substrate film having an initial elastic modulus in at least one direction of 2.5 - 10 GPa, an impact strength of 40 - 10000 J/mm and a thermal shrinkage in at least one direction at 150°C of -0.5% to 6%, and an easily adhesive coating layer on at least one surface of

the substrate film, and shows a haze of 0.001% to 7%.

【0008】

In this case, the thermal shrinkage in the longitudinal direction and the transverse direction of the substrate film at
5 150°C is each 0% to 4%.

【0009】

In this case, the substrate film is made of a polyester resin composition comprising 10 - 90 wt% of polyethylene terephthalate resin (A), and 90 - 10 wt% of a polybutylene
10 terephthalate resin and/or polytrimethylene terephthalate resin (B).

【0010】

In this case, the substrate film has a reduced viscosity of not less than 0.80.

15 **【0011】**

In this case, moreover, the easily adhesive coating layer can be composed of a coating solution containing at least binder (C) and hardener (D).

【0012】

20 In this case, moreover, the film is obtained by applying a coating solution for forming the aforementioned easily adhesive coating layer, and then subjecting the resulting film to at least uniaxial orientation.

【0013】

25 In this case, moreover, the polyester film can be used as a packaging material.

【Effect of the Invention】

【0014】

The present invention can provide a polyester film
30 which is superior in the mechanical strength, heat resistance, chemical resistance, insulation property and dimensional stability, and can be applied to fields associated with boiling or retort treatment, which require tenacity, pinhole resistance, bending resistance, bag breakage resistance on

dropping, impact resistance and the like, fields requiring thermoforming or vacuum forming, and various uses such as packaging bags for water-containing food, pharmaceutical products and the like.

5 **【Best Mode for Embodying the Invention】**

【0015】

The polyester film of the present invention has a substrate film having an initial elastic modulus in at least one direction of 2.5 - 10 GPa, an impact strength of 40 - 10000
10 J/mm and a thermal shrinkage in at least one direction at 150°C of -0.5% to 6%, and an easily adhesive coating layer on at least one surface of the substrate film, and shows a haze of 0.001% to 7%.

【0016】

15 The substrate film forming the polyester film of the present invention has an initial elastic modulus in at least one direction of 2.5 - 10 GPa, preferably 2.7 - 10 GPa, more preferably an initial elastic modulus in the longitudinal direction and the transverse direction of 2.7 - 10 GPa. When
20 it is less than 2.5 GPa, the film may be broken during high speed printing, printing displacement may occur and handling of the film in the form of a bag becomes difficult. When it exceeds 10 GPa, the producibility of the film becomes poor.

【0017】

25 The substrate film forming the polyester film of the present invention shows an impact strength of 40 - 10000 J/mm, preferably 60 - 1000 J/mm. When it is less than 40 J/mm, the film in the form of a bag filled with the contents may gets broken when dropped and the like. When it exceeds 10000 J/mm,
30 the producibility of the film becomes poor.

【0018】

The substrate film forming the polyester film of the present invention has a thermal shrinkage in at least one direction at 150°C of -0.5% to 6%, preferably 0% to 4%, more

preferably 0% to 1.5%. When it is lower than -0.5% or exceeds 6%, deformation of the film unpreferably occurs in the post-printing drying and the like.

【0019】

5 In addition, the polyester film of the present invention has a haze of 0.001% to 7%, preferably 0.01% to 5%. A haze of less than 0.001% degrades the slip property of the film and an elongated winding is not available. When the haze exceeds 7%, a defect occurs in that a print by back printing
10 becomes difficult to see.

【0020】

The substrate film forming the polyester film of the present invention is preferably made of a polyester resin composition containing 10 - 90 wt% of polyethylene
15 terephthalate resin A, and 90 - 10 wt% of a polybutylene terephthalate resin and/or polytrimethylene terephthalate resin B. The polyester resin composition contains polyethylene terephthalate resin A (hereinafter sometimes to be abbreviated as resin A) in a proportion of 10 - 90 wt%, preferably 15 - 70
20 wt%, more preferably 20 - 49 wt%, and a polybutylene terephthalate resin and/or polytrimethylene terephthalate resin B (hereinafter sometimes to be abbreviated as resin B) in a proportion of 90 - 10 wt%, preferably 85 - 30 wt%, more preferably 80 - 51 wt%. When resin A is contained in a
25 proportion of more than 90 wt%, flexibility becomes insufficient. When resin B exceeds 90 wt%, stretchability of the film becomes poor due to the fast crystallization rate of resin B, causing easy breakage during film forming.

【0021】

30 The polyethylene terephthalate resin A to be used in the present invention preferably has a reduced viscosity of 0.55 - 1.20, more preferably 0.55 - 0.80. When the reduced viscosity is smaller than this range, a film having practical mechanical strength cannot be obtained easily, and when it

exceeds this range, the film forming property of the film is unpreferably degraded.

【0022】

The polyethylene terephthalate resin A to be used in
5 the present invention is preferably made of a homopolymer
mainly comprising terephthalic acid and ethylene glycol. As
long as the heat resistance and other properties are not
impaired, it may be a polyester copolymer wherein not more than
20 mol%, preferably 0.1 - 10 mol%, of a different acid
10 component or a glycol component is copolymerized.

【0023】

When the polyethylene terephthalate resin to be used in
the present invention is a copolymer, the following monomers
can be used as a copolymerizable component.

15 【0024】

As the dicarboxylic acid usable for copolymerization,
aromatic dicarboxylic acid is exemplified by isophthalic acid,
orthophthalic acid, naphthalene dicarboxylic acid, biphenyl
dicarboxylic acid and the like. Examples of aliphatic
20 dicarboxylic acid include succinic acid, adipic acid, azelaic
acid, sebacic acid, dodecanedioic acid, dimer acid and the
like, and examples of alicyclic dicarboxylic acid include 1,4-
cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic
acid, 1,2-cyclohexane dicarboxylic acid, acid anhydride thereof
25 and the like. Examples of dicarboxylic acid containing a
polymerizable unsaturated double bond include α,β -unsaturated
dicarboxylic acid (e.g., fumaric acid, maleic acid, maleic
anhydride, itaconic acid, citraconic acid), alicyclic
dicarboxylic acid containing an unsaturated double bond (e.g.,
30 2,5-norbornene dicarboxylic anhydride, tetrahydrophthalic
anhydride) and the like.

【0025】

As the glycol usable for copolymerization, aliphatic
glycol having 3 to 10 carbon atoms, alicyclic glycol having 6

to 12 carbon atoms and ether bond-containing glycol and the like can be mentioned. As the aliphatic glycol having 3 to 10 carbon atoms, 1,2-propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 5 3-methyl-1,5-pentanediol, 1,9-nonanediol, 2-ethyl-2-butylpropanediol and the like can be mentioned. As the alicyclic glycol having 6 to 12 carbon atoms, 1,4-cyclohexanedimethanol and the like can be mentioned.

[0026]

10 Furthermore, as the ether bond-containing glycol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, glycols obtained by adding ethylene oxide or propylene oxide to two phenolic hydroxyl groups of bisphenols (e.g., 2,2-15 bis(4-hydroxyethoxyphenyl)propane etc.) and the like can be mentioned.

[0027]

In addition, the polybutylene terephthalate resin and/or polytrimethylene terephthalate resin B to be used in the 20 present invention preferably has a reduced viscosity of 0.80 - 2.20. When the intrinsic viscosity is smaller than this range, a film having practical mechanical strength cannot be obtained easily, and when it exceeds this range, the film forming property of the film is unpreferably degraded.

25 **[0028]**

The polybutylene terephthalate resin to be used in the present invention is preferably made of a homopolymer mainly comprising terephthalic acid and butanediol. As long as the heat resistance and other properties are not impaired, it may 30 be a polyester copolymer wherein not more than 20 mol%, preferably not more than 10 mol%, of a different acid component or a glycol component is copolymerized. In addition, the polytrimethylene terephthalate resin is preferably made of a homopolymer mainly comprising terephthalic acid and

trimethylene glycol, but it may be a polyester copolymer wherein not more than 20 mol%, preferably 0.1 - 10 mol%, of a different acid component or a glycol component is copolymerized.

5 **【0029】**

When the polybutylene terephthalate resin or polytrimethylene terephthalate resin to be used in the present invention is a copolymer, the following monomers can be used as a copolymerizable component.

10 **【0030】**

As the dicarboxylic acid usable for copolymerization, various dicarboxylic acids can be mentioned. Of these, examples of aromatic dicarboxylic acid include isophthalic acid, orthophthalic acid, naphthalene dicarboxylic acid, biphenyl dicarboxylic acid and the like. Examples of aliphatic dicarboxylic acid include succinic acid, adipic acid, azelaic acid, sebacic acid, dodecanedioic acid, dimer acid and the like, and examples of alicyclic dicarboxylic acid include 1,4-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, acid anhydride thereof and the like. Examples of dicarboxylic acid containing a polymerizable unsaturated double bond include α,β -unsaturated dicarboxylic acid (e.g., fumaric acid, maleic acid, maleic anhydride, itaconic acid, citraconic acid), alicyclic dicarboxylic acid containing an unsaturated double bond (e.g., 2,5-norbornene dicarboxylic anhydride, tetrahydrophthalic anhydride) and the like.

25 **【0031】**

As the glycol usable for copolymerization, aliphatic glycol having 2 to 10 carbon atoms, alicyclic glycol having 6 to 12 carbon atoms, ether bond-containing glycol and the like can be mentioned. As the aliphatic glycol having 2 to 10 carbon atoms, ethylene glycol, 1,2-propylene glycol, trimethylene glycol, 1,4-butanediol, 1,5-pentanediol, neopentyl

glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,9-nonanediol, 2-ethyl-2-butylpropanediol and the like can be mentioned. As the alicyclic glycol having 6 to 12 carbon atoms, 1,4-cyclohexanedimethanol and the like can be mentioned.

5 **【0032】**

Furthermore, as the ether bond-containing glycol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, glycols obtained by adding ethylene oxide or propylene
10 oxide to two phenolic hydroxyl groups of bisphenols (e.g., 2,2-bis(4-hydroxyethoxyphenyl)propane etc.) and the like can be mentioned.

【0033】

The substrate film forming the polyester film of the
15 present invention can contain any amount of fine particles in a polyester resin composition constituting the polyester film. For example, silicon dioxide, kaolin, clay, calcium carbonate, calcium terephthalate, aluminum oxide, titanium oxide, calcium phosphate, silicone particles and the like can be mentioned,
20 with preference given to inorganic lubricants. During melt mixing, additives such as stabilizer, coloring agent, antioxidant, antifoaming agent, antistatic agent and the like can be added as necessary besides lubricant.

【0034】

25 The polyester film of the present invention should have mechanical strength for the stability during processing such as printing and the like. For this end, polyethylene terephthalate resin A, and polybutylene terephthalate resin and/or polytrimethylene terephthalate resin B constituting the
30 substrate of the polyester film preferably do not allow copolymerization during melt extrusion. As a method for suppressing copolymerization, (1) a method comprising adding a particular phosphorus compound to suppress transesterification reaction, (2) a method comprising controlling the size of the

resin pellets to be mixed so as to prevent smooth mixing, (3) a method comprising lowering the temperature of extruder to prevent easy progression of transesterification, (4) a method comprising using an extruder having a double flight type screw so as to prevent smooth mixing of resin A and resin B, (5) a method comprising melt extrusion of each of resin A and resin B from two extruders, mixing them in a molten state immediately before extruding from a T-die and then extruding the mixture from the T-die and the like can be mentioned.

10 **【0035】**

When a phosphorus compound is added to suppress copolymerization of polyethylene terephthalate resin A and resin B which is either a polybutylene terephthalate resin or a polytrimethylene terephthalate resin during melt extrusion, it is preferable, but not limited, to use a phosphorus compound having a melting point of not less than 200°C and a molecular weight of not less than 200. While the optimal amount of addition varies depending on the kind of the phosphorus compound, polymerization conditions and the like, addition in a proportion of 0.01 - 0.3 wt% is preferable for the suppression of transesterification reaction between resin A and resin B. For use for food such as beverage can and the like, the compound and amount thereof should meet the standard of FDA (U.S. Food and Drug Administration), Japan Hygienic Olefin and Styrene Plastics Association and the like. To increase crystallization rate, it is also preferable to add a substance to be a nucleating agent for crystallization, while suppressing copolymerization.

25 **【0036】**

30 The substance to be a nucleating agent for crystallization can be added after mixing with a plasticizer such as polyethylene, polypropylene, polystyrene, polyester polymer or polyester copolymer having a molecular weight of not more than 20000, which has the aforementioned monomer

constitution, fatty acid ester and the like. As the nucleating agent for crystallization, inorganic particles of calcium carbonate, non-crystalline zeolite particles, anatase type titanium dioxide, rutile type titanium dioxide, calcium
5 phosphate, silica, kaolin, talc, clay, barium sulfate, zinc oxide, zinc sulfide and the like can be mentioned, which are generally added in a proportion of 0.001 - 2 wt%, preferably 0.01 - 1 wt%. However, the results thereof vary drastically depending on the substances to be added, the amount of
10 addition, means of addition, order of addition, particle size and the like, as well as the melt extrusion conditions of the film. Thus, for stable expression of the effect, it is preferable to employ a method comprising preparing master batch pellets by the addition of inorganic particles during
15 polymerization to a polyester copolymer having a molecular weight of not more than 20000 and having the aforementioned monomer constitution, dry blending the pellets with at least the pellets of resin A and resin B to be the substrate or master batch pellets, and melting and extruding the mixture.
20 As compared to the addition of inorganic particles to resin A and resin B during polymerization, dispersibility in a resin mixture becomes fine, which, it is considered, in turn increases crystallization rate and suppresses whitening of polyester film during boiling, retort treatment and
25 thermoforming.

【0037】

In addition, it is preferable to control the size of the resin pellets to be mixed, so as to suppress copolymerization of the polyethylene terephthalate resin A, and
30 a polybutylene terephthalate resin and/or polytrimethylene terephthalate resin B during melt extrusion.

【0038】

It is also preferable to set the temperature of each part to not more than 270°C, preferably not more than 262°C,

during the period of from mixing and melting of the resins, passage through an extruder, to extrusion from a T-die, so as to suppress copolymerization of the polyethylene terephthalate resin A, and a polybutylene terephthalate resin and/or
5 polytrimethylene terephthalate resin B during melt extrusion. The presence of a temperature zone exceeding 270°C in a melt extrusion step is considered to accelerate decomposition of a polyester usable as resin B, which in turn promote copolymerization of resin A and resin B. When the substrate
10 film forming the polyester film of the present invention is to be produced using a single extruder, in the melt extrusion step, resin A, resin B and other resin pellets constituting the aforementioned polyester resin composition are mixed, cast in an extruder, melted, extruded from a T-die, adhered to a
15 cooling roll by an electrostatic adhesion method and the like, and solidified by cooling to give a non-oriented sheet. In this case, the temperature of an extruder is preferably set to not more than 270°C, preferably not more than 262°C, for all of the feeding part, compression part, measuring part, filter,
20 resin flow path and T-die of the extruder.

【0039】

In general, when the extrusion temperature conditions for resin are described in literatures, the resin temperature immediately before entry of the resin into a T-die or
25 immediately after delivery of the resin from the T-die is often taken as the temperature condition of extrusion. Control of only the resin temperature immediately before entry into a T-die or immediately after delivery from the T-die is insufficient to definitely control the resin temperature during
30 the melt extrusion step up to the T-die. It is a general practice to intentionally change the feeding part, compressing part, measuring part, filter and resin flow path of an extruder, in view of the specific condition of the machine, such as screw shape of the extruder and the like, production

speed and stability, and the temperature of the respective parts is in fact often different from each other.

【0040】

Furthermore, when the substrate film forming the
5 polyester film of the present invention is to be produced using
a single extruder, so as to suppress copolymerization of
polyethylene terephthalate resin A, and a polybutylene
terephthalate resin and/or polytrimethylene terephthalate resin
B during melt extrusion, a uniaxial extruder having a double
10 flight type screw compression part (compression zone), which is
of a rapid compression type with a small compression ratio (not
more than 2.0) is preferably used. As an extruder having a
double flight type screw, UB series manufactured by Mitsubishi
Heavy Industries, Ltd. can be mentioned.

15 【0041】

To suppress copolymerization of polyethylene
terephthalate resin A, and a polybutylene terephthalate resin
and/or polytrimethylene terephthalate resin B during melt
extrusion, moreover, resin A and resin B are respectively
20 melted and extruded from two extruders, mixed in a molten state
and immediately thereafter extruded from a T-die to give the
substrate film forming the polyester film of the present
invention. As a method for mixing in a molten state
immediately before extrusion from a T-die, a method comprising
25 feeding respective molten resins in a molten state to molten
resin mixers such as extruders, static mixers and the like,
melt-mixing and extruding them, and the like can be mentioned.
As a device for mixing molten resins, conventional uniaxial
extruder, biaxial extruder, dynamic mixer, static mixer
30 (manufactured by Noritake Co., Limited and the like) and the
like can be mentioned. As a preferable method for suppressing
copolymerization of polyethylene terephthalate resin A and
polytrimethylene terephthalate resin B during melt extrusion,
the above-mentioned method (5), and a combination of method (5)

and other method can be mentioned.

【0042】

While the substrate film forming the polyester film of the present invention can be used when it meets the
5 requirements of a non-oriented sheet of the present invention, it can be preferably obtained by orienting a non-oriented sheet at least uniaxially, more preferably biaxially or more. The method of orientation includes tubular orientation, pantographic simultaneous biaxial orientation, linear motor
10 simultaneous or sequential biaxial orientation, sequential biaxial orientation based on a combination of a heating roll and a tenter and the like. In the case of sequential biaxial orientation, orientation methods of longitudinal-transverse, transverse-longitudinal, longitudinal-longitudinal-transverse,
15 longitudinal-transverse-longitudinal, longitudinal-transverse-transverse, longitudinal-longitudinal-longitudinal-transverse and the like can be mentioned.

【0043】

The production method of the film of the present
20 invention is shown below by referring to a sequential biaxial orientation method as an example. Resin chips of polyethylene terephthalate resin A, and a polybutylene terephthalate resin and/or polytrimethylene terephthalate resin B are mixed, cast into one extruder, melted, mixed and extruded. The mixture is
25 extruded from a T-die and the melt extruded sheet is electrostatically adhered to a chill roll to give a non-oriented sheet. The temperature of the chill roll then is preferably 10 - 40°C. When the temperature of the chill roll exceeds 40°C, the polybutylene terephthalate resin and/or
30 polytrimethylene terephthalate resin B crystallize to whiten the extruded sheet. As a result, haze after biaxial orientation becomes poor and the printed layer becomes difficult to see.

【0044】

The obtained non-oriented sheet is delivered to a pair of orienting rolls at 50 - 100°C with different speeds, drawn 2.5 to 5-fold in the longitudinal direction. The longitudinally oriented sheet is delivered to a tenter and
5 drawn 2.5 to 5-fold in the transverse direction at 60 - 120°C. Where necessary, the sheet may be drawn in the longitudinal direction and the transverse direction in two steps at different temperature and different folding rate. Then, the sheet is heat set at 180 - 230°C to give the substrate film
10 forming a polyester film.

【0045】

The substrate film used for forming the polyester film of the present invention needs to have an easily adhesive coating layer, preferably an easily adhesive coating layer
15 comprising binder C and hardener D, on at least one surface thereof. When an easily adhesive coating layer is not formed, adhesiveness of the printing ink may be degraded, and adhesion of a metal or inorganic oxide vapor-deposited layer becomes insufficient, thus degrading the stability of gas barrier
20 property. Particularly, when bags filled with food or liquid are sealed, and many of such bags are boil-treated with circulation during a boiling treatment, a vapor-deposited layer is easily detached in the absence of an easily adhesive coating layer, and the gas barrier property becomes unstable.

25 **【0046】**

As a method for forming an easily adhesive coating layer in the present invention, conventional coating methods can be used. For example, gravure coating, micro gravure coating, bar coating, reverse roll coating, reverse kissroll
30 coating, comma coating, dam coating, curtain coating, dip coating, blade coating and the like can be employed.

【0047】

In the present invention, a film after stretching film forming can also be coated. Preferably, however, a method

including applying a coating solution to an unoriented sheet during film forming and then subjecting the film to biaxial stretching, more preferably, a method including applying to a sheet after monoaxial stretching and then stretching the film
5 in the orthogonal direction thereof is employed.

【0048】

Preferable examples of binder C forming the easily adhesive coating layer usable in the present invention include polyester resin, polyurethane resin, polyacryl resin, polyvinyl
10 alcohol resin and copolymers thereof, ethylene-vinyl acetate copolymer resin and the like. To improve adhesion between a substrate film forming the polyester film and ink, a vapor-deposited layer and the like, a polyester resin is preferable.

【0049】

15 The polyester resin as binder C to be used in the present invention is a water-insoluble polyester copolymer obtained by reacting mixed dicarboxylic acid of metal sulfonate group-containing dicarboxylic acid (0.5 - 15 mol%) and dicarboxylic acid free of metal sulfonate group (85 - 99.5
20 mol%) with a polyol component. As the above-mentioned metal sulfonate group-containing dicarboxylic acid, metal salts such as 5-sulfoisophthalic acid, 4-sulfophthalic acid, 4-sulfonaphthalene-2,7-dicarboxylic acid, 5[4-sulfophenoxy]isophthalic acid and the like can be mentioned.
25 Particularly preferred are sodium 5-sulfoisophthalate and sodium sulfoterephthalate. The metal sulfonate group-containing dicarboxylic acid component is used in a proportion of 0.5 - 15 mol%, desirably 2.0 - 10 mol%, relative to the entire dicarboxylic acid component. When it exceeds 15 mol%,
30 dispersibility in water is improved but water resistance of polyester copolymer is markedly degraded, and when it is less than 0.5 mol%, dispersibility in water is markedly degraded. While the dispersibility of the polyester copolymer in water varies depending on the kind, mixing ratio and the like of the

copolymerization component, the above-mentioned metal sulfonate group-containing dicarboxylic acid is preferably used in a small amount as long as its dispersibility in water is not impaired. As the dicarboxylic acid free of metal sulfonate group, aromatic, alicyclic and aliphatic dicarboxylic acids can be used. As the aromatic dicarboxylic acid, terephthalic acid, isophthalic acid, orthophthalic acid, 2,6-naphthalene dicarboxylic acid and the like can be mentioned. The aromatic dicarboxylic acid is preferably used in a proportion of not less than 40 mol% of the entire dicarboxylic acid component. When it is less than 40 mol%, the mechanical strength and water resistance of the polyester copolymer decreases. As the aliphatic and alicyclic dicarboxylic acids, succinic acid, adipic acid, sebacic acid, 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid and the like can be mentioned. Addition of these non-aromatic dicarboxylic acid component sometimes results in improved adhesiveness, but it generally degrades mechanical strength and water resistance of the polyester copolymer. The polyol component to be reacted with the above-mentioned mixed dicarboxylic acid is aliphatic glycol having 2 to 8 carbon atoms or alicyclic glycol having 6 to 12 carbon atoms. Specific examples thereof include ethylene glycol, 1,2-propylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol, P-xylylene glycol, diethylene glycol, triethylene glycol and the like. As polyether, polyethylene glycol, polypropylene glycol, polytetramethylene glycol and the like can be mentioned. In addition, an oxycarboxylic acid component such as p-oxyethoxybenzoic acid may be copolymerized.

【0050】

As the polyester resin of binder C, a polyester graft copolymer can also be used. In the present invention, the "graft formation" means introduction of a branch polymer made

of a polymer other than the main chain into a branch polymer main chain.

(polyester graft copolymer)

The graft polymerization is generally carried out by
5 reacting a hydrophobic copolymerizable polyester resin
dissolved in an organic solvent with at least one kind of
polymerizable unsaturated monomer using a radical initiator.
The reaction product after completion of the grafting reaction
includes a desired graft copolymer of hydrophobic
10 copolymerizable polyester and polymerizable unsaturated
monomer, hydrophobic copolymerizable polyester resin free from
graft formation and the above-mentioned unsaturated monomer
polymer not grafted to the hydrophobic copolymerizable
polyester. The polyester graft copolymer in the present
15 invention means not only the above-mentioned polyester graft
copolymer but also a reaction mixture containing hydrophobic
copolymerizable polyester unreactive therewith, polymer of
unsaturated monomer not grafted thereto and the like.

【0051】

20 In the present invention, polyester graft copolymer
obtained by graft polymerization of hydrophobic copolymerizable
polyester resin and at least one kind of polymerizable
unsaturated monomer preferably has an acid value of not less
than $600 \text{ eq}/10^6 \text{ g}$, more preferably not less than $1200 \text{ eq}/10^6 \text{ g}$.
25 When the graft copolymer has an acid value of less than $600 \text{ eq}/10^6 \text{ g}$, adhesion of the object graft copolymer-containing
layer of the present invention to a layer covered therewith
does not become sufficient.

【0052】

30 The weight ratio of the hydrophobic copolymerizable
polyester resin and the polymerizable unsaturated monomer,
which affords a desirable graft copolymer is desirably within
the range of polyester /polymerizable unsaturated monomer =
40/60 - 95/5, more desirably 55/45 - 93/7, most desirably 60/40

- 90/10. When the weight ratio of the hydrophobic copolymerizable polyester resin is less than 40 wt%, superior adhesiveness of the polyester resin cannot be exhibited. On the other hand, when the weight ratio of the hydrophobic
5 copolymerizable polyester resin is greater than 95 wt%, the defect of the polyester resin, i.e., blocking, easily occurs.
【0053】

The polyester graft copolymer to be used in the present invention is in the form of a solution or dispersion in an
10 organic solvent, or a solution or dispersion in an aqueous solvent. Particularly, a dispersion in an aqueous solvent, namely, an aqueous resin dispersion, is preferable in terms of work environment and coatability. Such aqueous dispersion resin can be generally obtained by graft polymerization of the
15 aforementioned hydrophobic copolymerizable polyester resin with at least one kind of hydrophilic polymerizable unsaturated monomer in an organic solvent, adding water and evaporating the organic solvent.

【0054】

20 The above-mentioned polyester graft copolymer preferably shows an average particle size of not more than 500 nm, particularly 10 - 500 nm, as measured by a laser scattering method, and a semitransparent to opalescent appearance. Graft copolymers having various particle sizes can be obtained by
25 controlling the polymerization method. The average particle size is preferably not more than 400 nm, more preferably not more than 300 nm, from the aspect of dispersion stability. When it exceeds 500 nm, the gloss of the surface of a coated film is degraded and so is the transparency. When it is less
30 than 10 nm, the object water resistance of the present invention is unpreferably degraded.

【0055】

The polymerizable unsaturated monomer grafted to a hydrophobic copolymerizable polyester resin is a hydrophilic

radical polymerizable monomer, which has a hydrophilic group or a group capable converting to a hydrophilic group later. As the hydrophilic group, carboxyl group, hydroxyl group, phosphoric acid group, phosphorous acid group, sulfonic acid group, amide group, quaternary ammonium salt group and the like can be mentioned. As a group capable of converting to a hydrophilic group, acid anhydride group, glycidyl group, chloro group and the like can be mentioned. Of these groups, a carboxyl group is preferable in view of the aqueous dispersibility and increased acid value of a graft copolymer. Thus, a polymerizable unsaturated monomer having a carboxyl group or a group capable of converting to a carboxyl group is preferable.

【0056】

The glass transition temperature of the polyester graft copolymer is not more than 30°C, preferably not more than 10°C. Use of a polyester graft copolymer having a glass transition temperature of not more than 30°C for the graft copolymer-containing layer affords a polyester film superior in adhesiveness. When the properties of the graft copolymer are outside the above-mentioned range, the effect of a graft copolymer-containing layer comprising a graft copolymer is not easily exhibited.

【0057】

(hydrophobic copolymerizable polyester resin)

In the present invention, the hydrophobic copolymerizable polyester resin should be essentially water insoluble, which means that the resin does not disperse or dissolve in water by itself. When a polyester resin that is dispersed or dissolved in water is used for graft polymerization, the object adhesiveness and water resistance of the present invention are degraded. The composition of the dicarboxylic acid component of the hydrophobic copolymerizable polyester resin is preferably aromatic dicarboxylic acid 60 -

99.5 mol%, aliphatic dicarboxylic acid and/or alicyclic dicarboxylic acid 0 - 40 mol%, dicarboxylic acid having a polymerizable unsaturated double bond 0.5 - 10 mol%. When the proportion of the aromatic dicarboxylic acid is less than 60
5 mol% or aliphatic dicarboxylic acid and/or alicyclic dicarboxylic acid are/is more than 40 mol%, the adhesion strength decreases.

【0058】

When the proportion of the dicarboxylic acid having a
10 polymerizable unsaturated double bond is less than 0.5 mol%, grafting of a polymerizable unsaturated monomer to a hydrophobic copolymerizable polyester resin does not proceed efficiently, and when it exceeds 10 mol%, the viscosity markedly increases after grafting reaction to unpreferably
15 prevents uniform progress of the reaction. More preferably, the proportion of the aromatic dicarboxylic acid is 70 - 98 mol%, the proportion of the aliphatic dicarboxylic acid and/or alicyclic dicarboxylic acid is 0 - 30 mol%, and the proportion of the dicarboxylic acid having a polymerizable unsaturated
20 double bond is 2 - 7 mol%.

【0059】

The urethane resin U usable in the present invention as binder C for forming an easily adhesive coating layer is heat reactive water-soluble urethane wherein a terminal isocyanate
25 group is blocked with a hydrophilic group. As blocking agent for isocyanate group, a number of compounds such as bisulphites, and phenols, alcohols, lactams, oximes and active methylene compounds, each containing a sulfone group, and the like can be used. The blocked isocyanate group can be removed
30 by making the urethane prepolymer hydrophilic or water soluble, and the blocking agent can be removed by drying or heat setting during film production and the like. When thermal energy is applied to the resin U having a blocked isocyanate group, the blocking agent is released from the isocyanate group and the

resin U is self-crosslinked. Since resin U used for preparing a coating solution is hydrophilic, water resistance becomes poor. However, after coating, drying and heat setting to complete the thermal reaction, a coated film having fine water resistance can be obtained since the hydrophilic group of the urethane resin U is released. Of the above-mentioned blocking agents, one having adequate heat treatment temperature and heat treatment time and permitting industrial wide use, bisulphites are preferable. As the chemical composition of a urethane prepolymer usable for the above-mentioned resin U, (1) a compound having not less than two active hydrogen atoms in a molecule and a molecular weight of 200 - 20,000, (2) organic polyisocyanate having not less than two isocyanate groups in a molecule, and, in some cases, (3) a compound having a terminal isocyanate group obtained by reacting a chain extender having at least two active hydrogen atoms in a molecule can be mentioned. As the compound of the above-mentioned (1), compounds having not less than two hydroxyl groups, carboxyl groups, amino groups or mercapto groups in the terminal or in a molecule are generally known, and as particularly preferable compounds, polyether polyol, polyester polyol, polyetherester polyol and the like can be mentioned. As the polyether polyol, for example, alkylene oxides (e.g., ethylene oxide and propylene oxide), a compound wherein styrene oxide, epichlorohydrin and the like are polymerized, a compound obtained by random copolymerization, block copolymerization or addition polymerization to polyol thereof, and the like can be mentioned. As the polyester polyol and polyetherester polyol, linear or branched compounds can be mainly mentioned. They can be obtained by condensation with succinic acid, adipic acid, phthalic acid, acid anhydride and the like, saturated or unsaturated alcohols (e.g., ethylene glycol, diethylene glycol, 1,4-butanediol, neopentyl glycol, 1,6-hexanediol, trimethylolpropane etc.), polyalkyleneether glycols having

relatively low molecular weight (e.g., polyethylene glycol, polypropylene glycol etc.), or mixtures thereof. In addition, polyesters obtained from lactone and hydroxy acid can also be used as polyester polyol, and polyether esters obtained by
5 adding ethylene oxide, propylene oxide and the like to polyesters produced in advance can also be used as polyetherester polyol. As the organic polyisocyanate of the above-mentioned (2), isomers of toluylene diisocyanate, aromatic diisocyanates (e.g., 4,4-diphenylmethane diisocyanate
10 etc.), aromatic aliphatic diisocyanates (e.g., xylylene diisocyanate etc.), alicyclic diisocyanates (e.g., isophorone diisocyanate, 4,4-dicyclohexylmethane diisocyanate etc.), aliphatic diisocyanates (e.g., hexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate etc.), and
15 polyisocyanates obtained by addition of trimethylolpropane and the like to these compounds (single or multiple) can be mentioned. As the chain extender having at least two active hydrogens of the above-mentioned (3), glycols (e.g., ethylene glycol, diethylene glycol, 1,4-butanediol, 1,6-hexanediol
20 etc.), polyols (e.g., glycerol, trimethylolpropane, pentaerythritol etc.), diamines (e.g., ethylenediamine, hexamethylenediamine, piperazine etc.), amino alcohols (e.g., monoethanolamine, diethanolamine etc.), thiodiglycols (e.g., thiodiethylene glycol etc.), and water can be mentioned.

25 **【0060】**

In addition, the polyacryl resin can be obtained by polymerization of acrylic acid or a derivative thereof and, where necessary, a monomer other than acrylic acid (derivative) and having a vinyl group. As the monomer to be used, for
30 example, acrylic acid, methacrylic acid (hereinafter (meth)acrylic acid includes acrylic acid and/or methacrylic acid), lower alkyl ester of (meth)acrylic acid (e.g., methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, 2-ethylhexyl ester), methyl methacrylate, hydroxymethyl acrylate, styrene,

glycidyl methacrylate, methyl acrylate, ethyl acrylate and the like can be mentioned.

[0061]

In the present invention, the easily adhesive coating
5 layer preferably contains hardener D. As the hardener D, a phenol formaldehyde resin which is a condensate of alkylated phenols with formaldehyde, cresols etc. with formaldehyde; addition product of urea, melamine, benzoguanamine etc. with formaldehyde, an amino resin comprising the addition product
10 and an alkyl ether compound comprising an alcohol having 1 to 6 carbon atoms; a multifunctional epoxy compound; a multifunctional isocyanate compound; a block isocyanate compound; a multifunctional aziridine compound; an oxazoline compound and the like can be used. As the phenol formaldehyde
15 resin, for example, condensates of phenols such as alkylated (methyl, ethyl, propyl, isopropyl or butyl) phenol, p-tert-amylphenol, 4,4'-sec-butylidenephphenol, p-tert-butylphenol, o-, m-, p-cresol, p-cyclohexylphenol, 4,4'-isopropylidenephphenol, p-nonylphenol, p-octylphenol, 3-pentadecylphenol, phenol,
20 phenyl-o-cresol, p-phenylphenol, xylenol and the like and formaldehyde can be mentioned.

[0062]

As the amino resin, for example, methoxymethylol urea, methoxymethylol N,N-ethyleneurea, methoxymethylol
25 dicianediamide, methoxymethylol melamine, methoxymethylol benzoguanamine, butoxymethylol melamine, butoxymethylol benzoguanamine and the like can be mentioned, with preference given to methoxymethylol melamine, butoxymethylol melamine, methylol benzoguanamine and the like can be mentioned.

30 **[0063]**

As the multifunctional epoxy compound, for example, diglycidyl ether of bisphenol A and oligomer thereof, diglycidyl ether of hydrogenated bisphenol A and oligomer thereof, diglycidyl orthophthalate, diglycidyl isophthalate,

diglycidyl terephthalate, diglycidyl p-oxybenzoate, diglycidyl tetrahydrophthalate, diglycidyl hexahydrophthalate, diglycidyl succinate, diglycidyl adipate, diglycidyl sebacate, ethyleneglycol diglycidyl ether, propyleneglycol diglycidyl ether, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether and polyalkyleneglycol diglycidyl ethers, triglycidyl trimellitate, triglycidylisocyanurate, 1,4-diglycidylloxybenzene, diglycidylpropyleneurea, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, pentaerythritol triglycidyl ether, triglycidyl ether of glycerolalkyleneoxide adduct and the like can be mentioned.

【0064】

As the multifunctional isocyanate compound, low molecular weight or high molecular weight aromatic or aliphatic diisocyanate, and polyisocyanate of trivalent or more can be used. As the polyisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, toluene diisocyanate, diphenylmethane diisocyanate, hydrogenated diphenylmethane diisocyanate, xylylene diisocyanate, hydrogenated xylylene diisocyanate, isophorone diisocyanate, and trimers of these isocyanate compounds can be mentioned. In addition, a terminal isocyanate group-containing compound obtained by reacting the above isocyanate compound in an excess amount and a low molecular weight active hydrogen compound (e.g., ethylene glycol, propylene glycol, trimethylolpropane, glycerol, sorbitol, ethylenediamine, monoethanolamine, diethanolamine, triethanolamine etc.) or a high molecular weight active hydrogen compound such as polyesterpolyols, polyetherpolyols, polyamides and the like can be mentioned.

30 【0065】

The blocked isocyanate can be prepared by addition reaction of the above-mentioned isocyanate compound and a blocking agent by a conventionally known appropriate method. As the isocyanate blocking agent, for example, phenols such as

phenol, cresol, xyleneol, resorcinol, nitrophenol, chlorophenol etc.; thiophenols such as thiophenol, methylthiophenol etc.; oximes such as acetoxime, methylethylketoxime, cyclohexanoneoxime etc.; alcohols such as methanol, ethanol, 5 propanol, butanol etc.; halogen-substituted alcohols such as ethylenechlorohydrin, 1,3-dichloro-2-propanol etc.; tertiary alcohols such as t-butanol, t-pentanol etc.; lactams such as ϵ -caprolactam, δ -valerolactam, γ -butyrolactam, β -propyllactam etc.; aromatic amines; imides; active methylene compounds such 10 as acetylacetone, acetoacetic ester, ethyl malonate etc.; mercaptans; imines; ureas; diaryl compounds; sodium bisulfite and the like can be mentioned.

【0066】

These crosslinking agents D can be used alone or a 15 combination of two or more kinds thereof. The amount of the crosslinking agent D to be added is preferably 10 - 150 parts by weight, more preferably 20 - 120 parts by weight, per 100 parts by weights of binder C. When it is less than 10 parts by weight, a sufficient crosslinking effect is not expressed. 20 Therefore, delamination and breakage of vapor-deposited film occur during boiling treatment and the gas barrier property after boiling treatment becomes defective. When it exceeds 150 parts by weight, drawing after coating becomes difficult and a film having an easily adhesive coating layer becomes difficult 25 to obtain.

【0067】

In the present invention, the easily adhesive coating layer may contain particles, antistatic agent, surfactant, antioxidant, light shielding agent, antigelling agent and the 30 like.

【0068】

In the present invention, to prevent degradation of water resistance of the easily adhesive coating layer and gas barrier property after boiling treatment due to delamination

and breakage of vapor-deposited film during boiling treatment, which is caused by hardener D or self-crosslinking type resin, sufficient heat needs to be applied to perform crosslinking. However, when a film after the completion of biaxial
5 orientation is to be coated, the heat sufficient for crosslinking is difficult to apply in view of the stability of a substrate film used for forming a polyester film. Therefore, coating within the film forming step is preferable, where crosslinking can be carried out simultaneously with the heat
10 setting of the film, and a method comprising coating a sheet after uniaxial orientation is more preferable.

【0069】

In the present invention, preferable combination of binder C and crosslinking agent D is a polyester resin
15 copolymer and a melamine resin, a polyvinyl alcohol resin and a melamine resin, a polyester resin copolymer or an isocyanate resin, which is contained at least in the easily adhesive coating layer. A polyester graft copolymer that performs self-crosslinking can be used without a crosslinking agent, and is
20 preferable in view of producibility, blocking resistance and slippery property.

【0070】

In the present invention, to simultaneously improve haze, film forming stability and water resistance of the easily
25 adhesive coating layer and gas barrier property thereof after boiling treatment, which may be impaired by delamination and breakage of a vapor-deposited film during boiling treatment, a coating solution applied to a uniaxial orientation sheet is preferably led to a tenter after drying. Since the
30 polybutylene terephthalate resin and the polytriethylene terephthalate resin show a slower crystallization rate as compared to a polyethylene terephthalate resin, the transverse orientation temperature and the preheating temperature immediately before that need to be set higher, when the coating

solution is led to a tenter without drying, which causes easy occurrence of whitening due to crystallization (high haze) and breakage of the film. Therefore, an easily adhesive coating layer is preferably dried at 40 - 100°C after coating. When it
5 exceeds 100°C, crystallization of a uniaxial orientation sheet becomes noticeable and whitening and breakage are often caused. When it is less than 40°C, drying tends to become insufficient.

【0071】

In addition, and the rate of hot air is preferably
10 controlled in consideration of the producibility, and the stability of an easily adhesive coating layer. While it depends on the machine and a film forming rate, a hot air is preferably applied at 15 - 25 m/sec.

【0072】

15 The substrate film used for forming the polyester film of the present invention has a reduced viscosity of preferably 0.70 - 1.50, more preferably 0.80 - 1.10. When it is less than 0.70, insufficient flexibility leads to easy breakage of the vapor-deposited layer of metal or inorganic oxide during
20 practical use and the gas barrier lacks stability. When it exceeds 1.50, breakage unpreferably occurs frequently in the orientation step of the film.

【0073】

As a phosphorus compound that can be contained in the
25 substrate film forming the polyester film of the present invention, one having a melting point of not less than 200°C and a molecular weight of not less than 200 is preferable in consideration of the stability in an extruder. While the optimal amount of addition of such phosphorus compound varies
30 depending on the kind, in view of suppression of an ester exchange reaction thereof, it is preferably 0.01 - 0.3 wt%. For use for food such as beverage can and the like, the compound and amount thereof should meet the standards of FDA (U.S. Food and Drug Administration), Hygienic Polyolefin etc.

Association and the like.

【0074】

While the polyester film of the present invention can be produced by the aforementioned method, production thereof by
5 a different method is acceptable as long as the characteristics of the polyester film of the present invention are satisfied, and the method is not necessarily limited to those mentioned above.

【0075】

10 The thickness of the substrate film forming the polyester film of the present invention is preferably 3 - 1000 μm , more preferably 5 - 70 μm .

【0076】

A vapor-deposited metal layer or vapor-deposited
15 inorganic oxide layer can be formed on at least one surface of the easily adhesive coating layer of the polyester film of the present invention. As a metal preferable for forming a vapor-deposited metal layer, aluminum, palladium, zinc, nickel, gold, silver, copper, indium, tin, chrome, titanium and the like can
20 be mentioned. Representatively, aluminum is used. In addition, as an inorganic oxide preferable for forming a vapor-deposited inorganic oxide layer in the present invention, any can be used as long as a vapor-deposited layer of an inorganic oxide, which shows transparency and gas barrier property, can
25 be formed. Metal oxides and nonmetal oxides are widely used, and particularly, a vapor-deposited layer comprising silicon oxide and/or aluminum oxide as main components is preferable.

【0077】

The polyester film of the present invention can be
30 effectively utilized for use for which a nylon film is conventionally employed, which is specifically a food packaging material requiring pinhole resistance and bag breakage resistance, particularly, a packaging material for fish processed products involving a boiling treatment or a retort

treatment, pickles, daily dishes, livestock meat processed products and the like, based on the superiority of polyester in the heat resistance and moisture absorption dimensional stability. Moreover, it can be effectively utilized as
5 packaging for industrial materials such as pet food, agricultural chemicals, fertilizers, infusion pack, semiconductor, precision equipment and the like, as well as medical, electronic, chemical, mechanical products and the like. In addition, it is useful as a material of packaging
10 involving vacuum forming and air pressure forming, such as molded containers and the like, and a material of cards and electronic equipment cases, taking advantage of heat resistance, impact resistance and crystallization properties.

【Examples】

15 **【0078】**

The present invention is explained in detail in the following by referring to Examples. Each property value in the present invention was measured as shown below.

【0079】

20 1. Reduced viscosity (η_{sp}/c)

A polymer (0.125 g) was dissolved in phenol/tetrachloroethane = 6/4 (weight ratio) (25 mL) and measurement was performed at 25°C with a Ubbelohde viscometer. The unit was dL/g. The resin was in the form of chips, and the
25 film was cut finely and used for the measurement.

【0080】

2. Initial elastic modulus

The measurement was performed according to JIS-K7127-1989 using Autograph (manufactured by Shimadzu Corporation: AG-
30 5000A).

【0081】

3. Thermal shrinkage

A sample was cut into 10 mm X 150 mm, and gauge lines were marked at 100 mm intervals on 10 sample pieces. They were

left standing in a gear oven at 150°C for 30 min. without a load, after which they were taken out and the distance between gauge lines was measured at room temperature. The values were determined according to the following formula and an average
5 value of 10 sample pieces was taken as the thermal shrinkage (%) of each sample.

【0082】

thermal shrinkage = $((A-B)/A) \times 100$

A: distance between gauge lines before heating

10 B: distance between gauge lines after heating

【0083】

4. Haze

The measurement was performed based on JIS-K-7105-1981 and using a turbidity meter (manufactured by Nippon Denshoku
15 Industries Co., Ltd.: NDH2000), and the value of haze (HZ) shown thereon was used.

【0084】

5. Vision of printed matter

Using a three-color gravure printer manufactured by
20 Modern Machinery, Ltd., blue, red and white of gravure ink "UNIVURE A" manufactured by Dainippon Ink and Chemicals Incorporated were sequentially printed on one surface of an easily adhesive coating layer of the obtained polyester film having a vapor-deposited layer or coating layer by gravure
25 printing, and when the vision from the back surface was clear, ○ was indicated and when the vision was not clear, x was indicated. The printing was performed at a rate of 50 m/min, drying temperature 90°C.

【0085】

30 6. Gas barrier property

The polyester film having an easily adhesive coating layer, which was obtained in Example was fed to a vacuum vapor deposition apparatus using, as a vapor deposition source, particles (about 3 - 5 mm in size) of Al₂O₃ (purity 99.5%) and

SiO₂ (purity 99.9%). The inside of the chamber was maintained at a pressure of 1.5×10^{-5} Torr, and a mixture of oxides of SiO₂ (70 wt%) and Al₂O₃ (30 wt%) was evaporated by electron beam heating (15 kw) to form a colorless, transparent vapor-
5 deposited inorganic layer having a thickness of 220 Å on the easily adhesive coating layer. Thereafter, the oxygen transmission rate was measured using an oxygen transmission rate measurement apparatus (manufactured by ModernContorols: OX-TRAN 10/50A) at humidity 50%, temperature 25°C, wherein the
10 unit was mL/(m²·MPa·24hours). The water vapor transmission rate was measured using a water vapor transmission rate measurement apparatus (manufactured by ModernContorols: PERMATRAN) at humidity 0%, temperature 25°C, wherein the unit was g/(m²·24hours). In view of food packaging, an oxygen level of
15 not more than 50 mL/(m²·MPa·24 hours) was accepted and water vapor of not more than 5.0 g/(m²·24 hours) was accepted.

【0086】

7. Gas barrier property after boiling treatment

The samples (10 sheets, 15 cm X 15 cm) having a vapor-
20 deposited layer formed by the method of the above-mentioned (7.) were prepared, and immersed in hot water at 95°C for 30 min. with stirring in a 3 L container. The samples were left standing at 23°C, 65 RH% for 24 hr and the oxygen transmission rate and the water vapor transmission rate were measured in the
25 same manner as in (6.). In view of food packaging, an oxygen level of not more than 50 mL/(m²·MPa·24 hours) was accepted and water vapor of not more than 10 g/(m²·24 hours) was accepted.

【0087】

8. Bag dropping test

30 As a sealant film, a nonoriented polypropylene film (manufactured by Toyo Boseki Kabushiki Kaisha: P1153: 50 μm) was dry laminated on an easily adhesive coating layer of the obtained polyester film, and four sides were sealed with an impulse sealer. Ten bags (150 mm X 150 mm) containing water

were produced, subjected to a retort treatment at 125°C for 30 min. The bags were dropped 20 times from a height of 1 m at 5°C. The average number of bag droppings before incidence of bag breakage or water leakage was employed. Preferably, the number is not less than 10, more preferably not less than 15. When it is less than 10, practical problems are caused in the transportation of packages.

【0088】

9. Impact strength

Using a film impact tester (manufactured by Toyo Seiki Seisaku-sho, LTD.: serial number T-84-3), a measurement film was pressed with a clamp, thrust a 1/2 inch diameter hemisphere impacting head thereinto, and the impact strength of the sample was measured. Ten film samples were prepared, and the impact strength was measured for 5 films at a time, changing the surface to be subjected to the impact. The sample was cut into 100 mm X 100 mm or more, and the ring that pressed the sample had an inner diameter of 30 mm. Average values of the impact strength of sample pieces were determined, and converted to those per 1 mm of thickness to give the impact strength (J/mm) of the film.

【0089】

(Example 1)

(Preparation of coating solution)

A polyester aqueous dispersion (100 parts by weight, manufactured by Toyo Boseki Kabushiki Kaisha: MD1200, solid content 30 wt%), methyl melamine (40 parts by weight, manufactured by Sumitomo Chemical Co., Ltd.: M-30W), 20 wt% aqueous dispersion (20 parts by weight) of colloidal silica particles (manufactured by Nissan Chemical Industries, Ltd.: SnowTex OL, average particle size 40 nm), water (410 parts by weight), and isopropyl alcohol (50 parts by weight) were mixed to give a coating solution having a solid content concentration of 10%.

【0090】

(Formation of film)

Polyethylene terephthalate resin (A1) (reduced viscosity 0.75) comprising 2000 ppm of silicon dioxide (F) 5 (manufactured by FUJI SILYSIA CHEMICAL LTD.: Silysia 310) previously added during polymerization was prepared as resin A, polybutylene terephthalate resin (B1) (reduced viscosity 1.20) and polybutylene terephthalate resin (B2) (reduced viscosity 1.10) comprising 1% of an organic phosphorus compound 10 (manufactured by ASAHI DENKA Co., Ltd.: Adeka Stub PEP-45) were prepared as resin B, and polybutylene terephthalate (C1) (copolymerized monomers: terephthalic acid/sebacic acid//ethylene glycol/1,4-butanediol) (90/10//60/40 (molar ratio) molecular weight 2000) previously comprising 2% of talc 15 (D) (average particle size by electron microscope method 3.5 μm) during polymerization was prepared as polyester C. They were cast into a single screw extruder (screw 65 ϕ : UB manufactured by MITSUBISHI HEAVY INDUSTRIES, LTD.) at A1/B1/B2/C1 = 40/56/2/2 (parts by weight). For temperature 20 setting of the extruder, temperatures of a feeding part (Ex1), a compressing part (Ex2), a measuring part (Ex3), the flow path up to a filter, the filter part, the flow path up to a die, and the die of the extruder were set, where Ex1 was 240°C, from Ex2 to the filter part was 260°C, and thereafter was 255°C, and 25 resins were supplied. The temperature of the resins measured immediately after extrusion from the T-die was 258°C. A 200 mesh filter was used. The resins extruded from the T-die was rapidly cooled on a roll cooled to 20°C according to an electrostatic adhesion method to give a non-oriented sheet 30 having a thickness of about 200 μm . The sheet was supplied to a roll drawing machine, and drawn 3.3-fold in the longitudinal direction at 63°C. Then, a coating solution was applied with a wire bar and dried by blowing hot air at 70°C to the coated surface at 20 m/sec for 30 sec. Subsequently, the sheet was

transversely drawn 3.6-fold at 88°C in a tenter, and set *in situ* in the tenter at 200°C for about 10 sec and at 220°C for about 10 sec, while relaxing by 4% in the transverse direction to give an about 16 μm polyester film.

5 **【0091】**

 In addition, a polyester film having a colorless and transparent vapor-deposited layer made of a mixed inorganic oxide of SiO_2 and Al_2O_3 and having a thickness of 220 Å was obtained, which layer was formed on the surface of the easily
10 adhesive coating layer (coated layer) of the obtained polyester film. The properties of the obtained film were evaluated and are shown in Table 3.

【0092】

 (Example 2)

15 In the same manner as in Example 1 except that the mixing ratio of respective resins was set to A1/B1/B2/C1 = 75/21/2/2 (parts by weight), a polyester film and a polyester film having a vapor-deposited layer were obtained. The properties of the obtained films were evaluated and the results
20 are shown in Table 1.

【0093】

 (Example 3)

 In the same manner as in Example 1 except that the mixing ratio of respective resins was set to A1/B1/B2/C1 =
25 25/71/2/2 (parts by weight), a polyester film and a polyester film having a vapor-deposited layer were obtained. The properties of the obtained films were evaluated and the results are shown in Table 1.

【0094】

30 (Example 4)

 In the same manner as in Example 1 except that the coating solution was dried by blowing hot air at 90°C to the coated surface at 15 m/sec for 30 sec, a polyester film and a polyester film having a vapor-deposited layer were obtained.

The properties of the obtained films were evaluated and the results are shown in Table 1.

【0095】

(Comparative Example 1)

5 In the same manner as in Example 1 except that the coating solution was dried by blowing hot air at 110°C to the coated surface at 15 m/sec for 20 sec, a polyester film and a polyester film having a vapor-deposited layer were obtained. The properties of the obtained films were evaluated and the
10 results are shown in Table 1.

【0096】

(Comparative Example 2)

 In the same manner as in Example 1 except that the coating solution was dried by blowing hot air at 70°C to the
15 coated surface at 35 m/sec for 30 sec, a polyester film and a polyester film having a vapor-deposited layer were obtained. The properties of the obtained films were evaluated and the results are shown in Table 1.

【0097】

20 (Example 5)

 In the same manner as in Example 3 except that the coating solution was prepared as shown in the following, a polyester film and a polyester film having a vapor-deposited layer were obtained.

25 **【0098】**

(Preparation of polyester copolymer)

 Dimethyl terephthalate (345 parts), 1,4-butanediol (211 parts), ethylene glycol (270 parts) and tetra-n-butyl titanate (0.5 part) were charged in a stainless steel autoclave equipped
30 with a stirrer, a thermometer and a partial reflux condenser, and transesterification reaction was carried out from 160°C to 220°C over 4 hr. Then, fumaric acid (14 parts) and sebacic acid (160 parts) were added, and the temperature was raised from 200°C to 220°C over 1 hr to carry out esterification

reaction. The temperature was raised to 255°C, the reaction system was gradually depressurized, and the reaction was carried out under reduced pressure of 0.22 mmHg for 1.5 hr to give a polyester copolymer. The obtained polyester was pale-
5 yellow and transparent and had a weight average molecular weight of 20000.

【0099】

(Self-crosslinking polyester graft copolymer)

The above-mentioned polyester copolymer resin (75
10 parts), methyl ethyl ketone (56 parts) and isopropyl alcohol (19 parts) were charged in a reaction vessel equipped with a stirrer, a thermometer, a reflux condenser and a titration dropping device, and the resins were dissolved by heating and stirring at 65°C. After complete dissolution of the resins,
15 maleic anhydride (15 parts) was added to the polyester solution. Then, styrene (10 parts), and a solution of azobisdimethylvaleronitrile (1.5 parts) in methyl ethyl ketone (12 parts) were added dropwise to the polyester solution at 0.1 mL/min, and the mixture was further stirred for 2 hr. The
20 reaction solution was sampled for analysis, and methanol (5 parts) was added. Then, water (300 parts) and triethylamine (15 parts) were added to the reaction solution, and the mixture was stirred for 1 hr. Thereafter, the inside temperature of the reaction vessel was raised to 100°C, methyl ethyl ketone,
25 isopropyl alcohol and excess triethylamine were distilled away to give an aqueously dispersing graft polymerization resin. The aqueously dispersing graft resin was pale-yellow and transparent and had a glass transition temperature of -10°C.

【0100】

30 (Preparation of coating solution)

The aqueously dispersing graft resin and, as a polyester resin, an aqueous polyester resin obtained by copolymerization of terephthalic acid/isophthalic acid/5-sulfoisophthalic acid/ethylene glycol/1,4-butanediol at

25/20/5/25/25 (weight ratio) were diluted with water:isopropyl alcohol = 9:1 (weight ratio) to a weight ratio of 90:10, solid content concentration 10% and used as a coating solution. The properties of the obtained film were evaluated. The results
5 thereof are shown in Table 1.

【0101】

(Example 6)

In the same manner as in Example 3 except that polytrimethylene terephthalate resin having a reduced viscosity
10 of 0.83 was used instead of polybutylene terephthalate resin, a polyester film and a polyester film having a vapor-deposited layer was obtained. The properties of the obtained film were evaluated. The results thereof are shown in Table 1.

【0102】

15 (Comparative Example 3)

In the same manner as in Example 3 except that a coating solution was not applied, a substrate film for forming a polyester film and a film having a vapor-deposited layer were obtained. The properties of the obtained film were evaluated.
20 The results thereof are shown in Table 1.

【0103】

(Comparative Example 4)

In the same manner as in Example 1 except that the longitudinal orientation ratio was set to 2.5-fold and the
25 transverse orientation ratio was set to 2.5-fold, a polyester film and a film having a vapor-deposited layer were obtained. The properties of the obtained film were evaluated. The results thereof are shown in Table 1.

【0104】

30 (Comparative Example 5)

In the same manner as in Example 1 except that the temperatures of Ex1, Ex2, Ex3 and the flow path up to the filter, the filter part, the flow path up to the die, and the die of the extruder was set to 290°C for all of them, a

polyester film and a film having a vapor-deposited layer were obtained.

The properties of the obtained film were evaluated. The results thereof are shown in Table 1.

5

[0105]

[Table 1]

	reduced viscosity (dL/g)	initial elastic modulus (GPa) (longitudinal/transverse)	thermal shrinkage (%) (longitudinal/transverse)	haze (%)	appearance after printing	after vapor deposition		after vapor deposition, boil treatment		impact strength (J/mm)	bag drop test (times)
						oxygen transmission rate	water vapor transmission rate	oxygen transmission rate	water vapor transmission rate		
Ex. 1	0.85	2.7/2.8	2.5/1.1	3.8	O	12	2.5	24	3.3	71	17
Ex. 2	0.89	3.8/4.1	2.0/0.8	2.8	O	10	1.0	12	1.4	70	18
Ex. 3	0.97	3.1/3.2	1.9/0.7	2.0	O	14	1.8	16	2.1	72	18
Ex. 4	0.94	3.2/3.2	1.8/0.6	2.9	O	15	1.7	20	2.0	74	18
Comp. Ex. 1	0.93	3.1/3.2	2.1/0.9	9.4	x	82	33.5	241	not less than 20	73	17
Comp. Ex. 2	0.93	3.1/3.1	2.2/0.9	7.2	x	65	21.3	195	not less than 20	71	17
Ex. 5	0.95	3.0/3.2	1.9/0.8	2.9	O	12	1.2	15	1.9	73	18
Ex. 6	0.85	3.3/3.5	2.1/0.8	1.8	O	16	2.2	20	2.8	68	16
Comp. Ex. 3	0.94	3.1/3.2	1.8/0.6	1.2	O	35	4.2	380	not less than 20	71	16
Comp. Ex. 4	0.85	1.6/1.6	1.4/0.8	1.8	O	16	2.2	20	2.8	88	17
Comp. Ex. 5	0.71	2.7/2.7	1.8/0.6	1.2	O	35	4.2	380	not less than 20	28	3

Unit: oxygen transmission rate mL/(m²·MPa·24 hours), water vapor transmission rate g/(m²·24 hours)

【0106】

While the polyester film of the present invention has been described based on plural Examples in the above, the present invention is not limited to the constitutions described
5 in the Examples above, but rather, various changes may be made to the constitution as appropriate without departing from the gist of the present invention, such as appropriate combination of the constitutions described in respective Examples and the like.

10 【Industrial Applicability】

【0107】

As mentioned above, since the polyester film of the present invention is characteristically superior in mechanical strength, heat resistance, chemical resistance, insulation
15 property and thermal dimensional stability, it can be preferably used for the fields associated with boiling or retort treatment, which require tenacity, pinhole resistance, bending resistance, bag breakage resistance on dropping, impact resistance and the like, fields requiring thermoforming or
20 vacuum forming, and uses such as packaging bags for water-containing food, pharmaceutical products and the like.

【Document】 Abstract

【Summary】

【Problem】 Provision of a polyester film superior in mechanical strength, heat resistance, chemical resistance, insulation
5 property and thermal dimensional stability, and suitable for application to fields associated with boiling or retort treatment, which require tenacity, pinhole resistance, bending resistance, bag breakage resistance on dropping, impact resistance and the like, fields requiring thermoforming or
10 vacuum forming, and various uses such as packaging bags for water-containing food, pharmaceutical products and the like.

【Solving Means】 A polyester film characteristically comprising a substrate film having an initial elastic modulus in at least one direction of 2.5 - 10 GPa, an impact strength
15 of 40 - 10000 J/mm and a thermal shrinkage in at least one direction at 150°C of -0.5% to 6%, and an easily adhesive coating layer on at least one surface of the substrate film, which shows a haze of 0.001% to 7%.

【Main Drawing】 none